Electrochemical Synthesis of Architecture-Controlled Mesostructures

Scientific Achievement

We have recently developed a new technique for synthesizing three dimensional superconducting and magnetic meso and nano-structures with controlled shapes through electro-chemistry. By carefully manipulating the growth conditions, distinct shapes of lead crystals such as octahedra, hexagonal plates, triangular prisms, dodecahedra, single needles, tripods, and aligned brushes were fabricated. Many of these basic shapes can be further tuned in terminal shape, internal voids or branching behavior yielding, in the extreme, snowflake-like crystals. A supporting electrolyte having the right concentration of only boric acid, balanced with the concentration of a metal salt having specific counter ions, are some of the keys to growing these shapes. Besides providing crucial information for understanding the self-assembly process of nanocrystalline growth, these new three dimensional meso and nano-crystals provide a new direction for fundamental studies of superconductivity (vortex confinement in 3D and shape-tuning of the band structure) and catalysis (metal systems such as Pt, Pd, Fe and Cu where specific crystal faces or defects of single crystals are known to have drastically different activities and optimized composition for bianary and ternary catalysts such as Pt/Ru/Sn).

One of the greater difficulties in electrochemistry is achieving control of a 20+ dimension parameter space. In order to overcome this barrier, we have developed a system for combinatorial electrodeposition which allows reproducible control over all parameters simultaneously. The system will allow rapid characterization of many critical parameters relevant for shape-controlled meso/nano crystals. In addition, the system will be ideally suited for the synthesis of alloyed nano-crystals where high-level control of the secondary element can be achieved.

Significance

The extrinsic properties of nanocrystals are mainly determined by size, shape, composition, and crystallinity. By controlling the electrode potential in dilute, low ionic strength plating baths as outlined in *J Am Chem Soc*, **126,** 2316 (2004), one can control any one of these parameters to fine-tune the properties of nanocrystals in any size from under 200nm to over 10μm. Unlike most other methods for making shaped mesostructures, the results of our electrodeposition studies are untemplated, single or multiply twinned crystals. Such 3D crystals provide unique samples – unavailable by any other synthesis technique – for (i) exploring the nucleation of superconductivity in 3D nanostructures; (ii) altering the vortex shapes in quasi-fractal shaped meso-structures (iii) tailoring the band structure by size & shape, and (iv) changing the effective catalytic activity of nanocatalysts through shape control.

Performers

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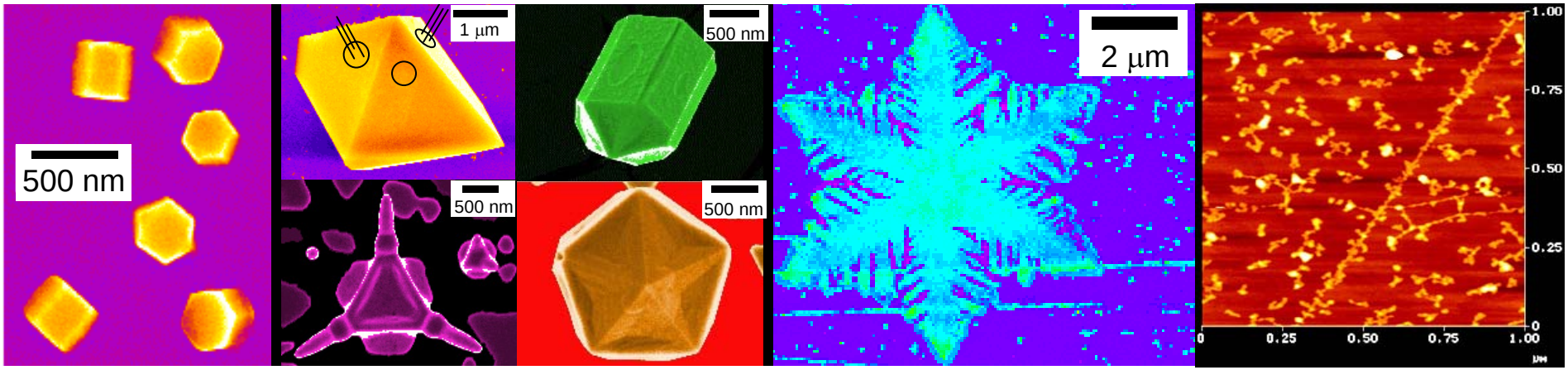
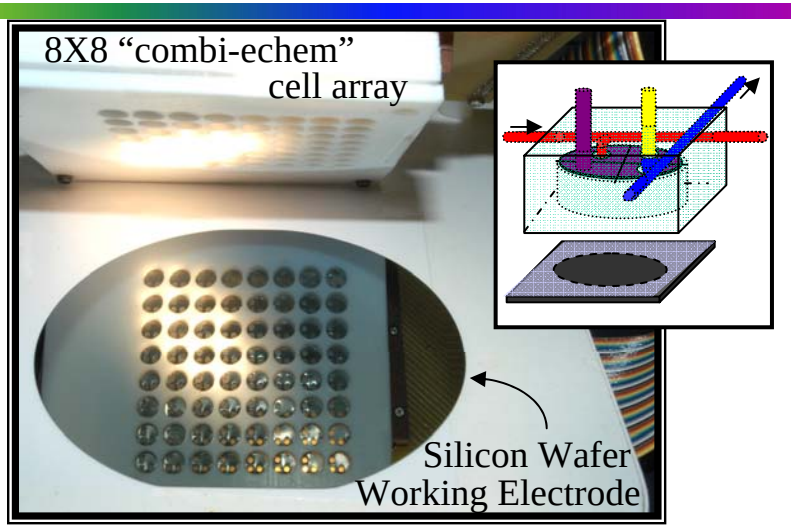


Cobalt | 3D Pb Meso-crystals | Fractal-like Pb snowflake | ZnS Nanowires

Combinatorial electrodeposition for rapid discovery and tuning of complex systems

- Phase space control: voltage, pH, concentration, temperature, additives, etc…
- Controlled alloying of meso and nano-structures
- Rapid design of new hybrid systems (SC/FE; SC/N)



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